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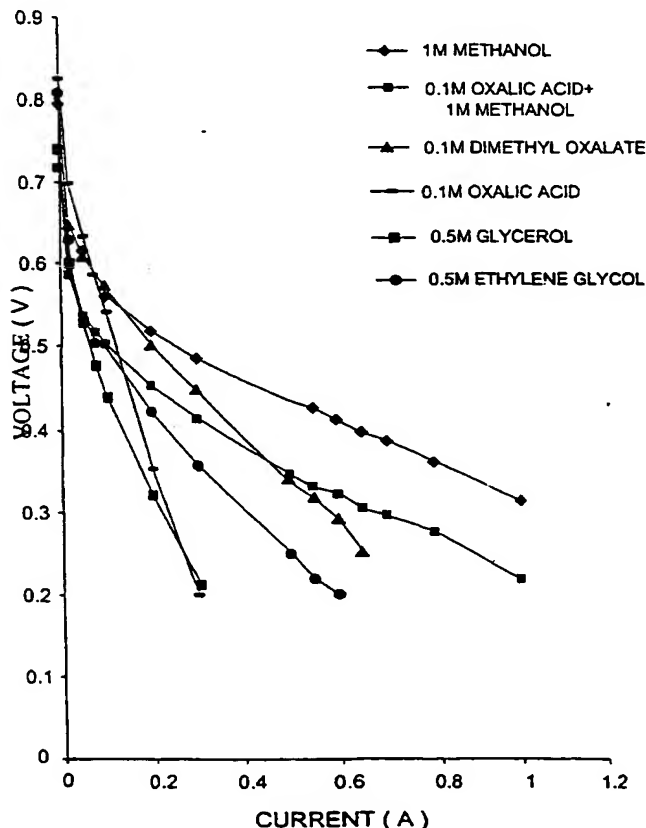
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(54) Title: NOVEL FUELS



(57) Abstract: Disclosed are the use of dimethyl oxalate, ethylene glycol, its oxalic, glyoxalic, and formic esters, glyoxylic acid and its methyl esters, glyoxylic aldehyde, and poly(ethylene oxalate) for fueling fuel cells, fuel cells fueled by these compounds, a hybrid power source containing these fuel cells, and a method for evaluating their concentration in solution.

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NOVEL FUELS

FIELD OF THE INVENTION

The invention relates to fuel cells and to organic fuels for use in fuel cells.

5 BACKGROUND OF THE INVENTION

Hydrocarbons and aliphatic alcohols are very difficult to electro-oxidize completely (J. Wang, S. Wasmus, and R. F. Savinell, *J. Electrochem. Soc.* **142**, 4218 (1995)), the main products of aliphatic alcohols oxidation being aldehydes or ketones, CO₂ and acids or esters. Even at 190°C, in a polymer-electrolyte
10 membrane (PEM) Fuel Cell, the oxidation of ethanol is incomplete, the main oxidation product (over 60%) is ethanal while CO₂ is less than 40% of the oxidation products. A compound which does not electro-oxidize in 80% or more cannot be considered an efficient fuel. To the best knowledge of the inventors there has never been a report on the complete electro-oxidation of a compound
15 having a C-C bond, except for oxalic acid (V. S. Bagotzky and Y. B. Vasilyev, *Electrochimica Acta* **9**, 869 (1964)). There are several publications that teach fuels for use in fuel cells. Among them US 5,599,638 mentions the use of methanol, formaldehyde, formic acid, dimethoxymethane, trimethoxymethane, and trioxane. In a screening of about 150 organic compounds as potential fuels
20 for fuel cells, which was carried out by NASA (NASA report No. SP-120 (1967), chapter 15, pp. 225 ff.) only methanol was checked for being an effective fuel. The other organic molecules were tested in acidic, neutral or basic solutions for their half cell potential, and the voltage of the electrode was measured at different currents and temperatures and the maximum power per cm² was calculated,
25 assuming a theoretical oxygen electrode. All the molecules that were screened showed some maximum power in the range 1 to 250 mW/cm². However, this parameter does not teach whether a compound is a good candidate as a fuel. For

example, methanol, which is considered a good organic fuel and ethanol, which can hardly be considered a fuel showed similar values of maximum power in acidic medium (13 and 15 mW/cm² respectively). It was reported in SP-120 (chapter 16, pp. 262 ff.) that ethylene glycol and urea performed poorly (in 30% KOH fuel cell). Some other molecules mentioned in this NASA report are glycerol, glyoxal aldehyde and glyoxylic acid.

SUMMARY OF THE INVENTION

The present invention provides organic fuels for fuel cells. The organic fuels according to the present invention are selected from the group consisting of dimethyl oxalate (DMO), ethylene glycol (EG), its oxalic, glyoxalic, and formic esters, glyoxylic acid and its methyl esters, glyoxylic aldehyde, and poly(ethylene oxalate), the latter being a polyester of oxalic acid and ethylene glycol. The organic fuels of the invention undergo clean and efficient oxidation in non-alkaline fuel cells, especially in acidic fuel cells. Preferable fuels according to the present invention are dimethyl oxalate, ethylene glycol, its formic acid ester, ethylene oxalate and poly(ethylene oxalate). Most preferable fuels according to the present invention are ethylene glycol and dimethyl oxalate. Preferable fuels of the invention are those that goes over 80% conversion to CO₂, and leave only negligible amounts of nonvolatile side products when used as fuels in a fuel cell.

Non-limiting examples of fuel cells that may work satisfactorily with the fuels of the invention are liquid feed fuel cells, gas feed fuel cells, high temperature fuel cells, solid oxide fuel cells, molten carbonate fuel cells, and fuel cells that use proton exchange or proton conducting membranes. Preferably, fuel cells that use proton exchange or proton conducting membranes, or solid oxide fuel cells.

The invention also provides for mixtures of the fuels of the inventions, as well as mixtures of the fuels of the invention with known organic fuels, such as methanol, for use as fuels in fuel cells.

Some of the fuels of the invention may also be useful with alkaline fuel
5 cells, especially in elevated temperatures. However, when alkaline electrolyte is used, there may be a need to replace it from time to time, due to incomplete electro-oxidation of the fuels in basic environment and the accumulation of carbonates or other organic salts due to this incomplete electro-oxidation.

When fuel cells operate with the fuels of the invention they exhibit
10 crossover current density which is lower than that the same fuel cells exhibit when operating with methanol, which is currently the most commonly used fuel in such cells. The low crossover current results in high efficiency. Without being bound to theory, it may be assumed that the low crossover currents are attributed to the large molecular size of the fuels of the invention, in comparison with that
15 of methanol. The large molecular size is correlated with a small diffusion coefficient, which leads to small crossover current density.

Furthermore, the fuels of the invention have higher boiling points than methanol, thus transporting through the proton conducting membrane mainly in their liquid phase. Naturally, the diffusion coefficient in liquid phase is smaller
20 than in the gas phase.

The solid fuels of the invention, such as DMO and poly(ethylene oxalate), may be advantageous over liquid fuels like methanol for several reasons such as their easier handling and their lower solubility in water. Thus, they maintain low concentration which helps in keeping the crossover current low. Furthermore, it is
25 possible to store saturated solutions thereof, for example, in the anode chamber of the fuel cell, together with considerable amount of solid fuel, which dissolves when the cell is in operation and fuel is consumed, while the non-dissolved solid fuel serves as a fuel reservoir.

In accordance with another of its aspects the invention provides a direct oxidation fuel cell having an anode, a cathode, a proton conducting membrane disposed between said anode and said cathode, means for supplying an organic fuel to the anode and means for supplying oxygen to the cathode, wherein said
5 organic fuel is selected from the group consisting of dimethyl oxalate (DMO), ethylene glycol (EG), its oxalic, glyoxalic, and formic esters, glyoxylic acid and its methyl esters, glyoxylic aldehyde, and poly(ethylene oxalate). Preferable cells according to this aspect of the invention are those wherein the fuels are selected from the group consisting of dimethyl oxalate, ethylene glycol, its oxalic and
10 formic acid esters, and poly(ethylene oxalate). Most preferable fuel cells according to this aspect of the present invention are those wherein the fuel is selected from the group consisting of ethylene glycol and dimethyl oxalate.

According to one embodiment, the fuel cell according to this aspect of the present invention is further characterized in that the CO₂ produced during the
15 operation thereof is released through a thin hydrophobic porous matrix placed in the anode compartment or in the fuel tank, thus allowing the release of the gas without losing solution.

According to another of its embodiments the present invention provides for a fuel cell, which is specifically adapted for working with the fuels of the
20 invention. Such a fuel cell is characterized by having a cathode comprising, in addition to oxygen reduction catalyst, a fuel oxidation catalyst, non-limiting examples thereof are Pt-Ru, Pt-Sn, Pt-Ru-Sn, Pt-Ag-Ru, Pt-Os catalyst, or combination of these catalysts. The fuel oxidation catalyst at the cathode improves oxidation of the fuel that crossed over the membrane and prevents it
25 from deactivating the oxygen reduction catalyst of the cathode, which typically is a Pt or Pt alloy catalyst. The practical ratio between the reduction catalyst to the oxidation catalyst is between 1% to 50%, preferably 5% to 20% (w/w) or between 0.01 to 5mg, preferably between 0.05 to 0.2mg oxidation catalyst per cm² of the oxygen electrode.

The invention further provides, according to another of its aspects, a method for evaluating the concentration of the new fuels in at a predetermined temperature, the method comprising the following steps:

- (a) preparing calibration curves of crossover current vs. fuel concentration
5 at said predetermined temperature in a fuel cell;
- (b) measuring the crossover current at said predetermined temperature in said fuel cell; and
- (c) evaluating the fuel concentration from the current measured in step (b) and the calibration curve prepared in step (a).

10 This method is based on the inventors finding that crossover current in fuel cells of the invention is directly proportional to the fuel concentration. For instance, the crossover current density of 1M EG at 80°C was found to be about twice that of 0.5M EG at the same temperature (41 and 19mA/cm², respectively) and the crossover current density of 0.25M DMO at 60°C was found to be about
15 2.5 times that of 0.1M DMO at the same temperature (2.5 and 0.9mA/cm², respectively). This finding is valid under conditions ensuring that the measured current is independent of the voltage at which it is measured.

The method of the invention may be applied to measure the fuel concentration of a fuel solution in a working fuel cell. This may be carried out by
20 measuring the crossover current in the operating fuel cell. Alternatively, an auxiliary small fuel cell for carrying out the measurement may be provided. This alternative allows for the measurement in accordance with the invention without having to operate the whole fuel cell in the voltage required for the measurement. The auxiliary fuel cell may be physically separated from the fuel cell, build in it,
25 attached to it or attached to the fuel tank.

The present invention also provides for a hybrid power source comprising at least one fuel cell according to the present invention a DC to DC converter, and a rechargeable battery.

Direct methanol fuel cell (DMFC) and liquid feed fuel cells (LFFC) are
30 low power sources. However, devices like cellular telephones, computers and

small electric vehicles need high power for short times. For these and for similar applications it is possible to combine a fuel cell according to the invention with a small high power rechargeable battery, which supplies the high power when required. Such a combination is advantageous over current art hybrid power source, *inter alia* thanks to the small crossover current. Today DC to DC converters can start working from 0.7V. As a it is possible to combine as few as two or three fuel cells (in a series combination) through a DC to DC converter to a battery. If the crossover current density is small enough, say 15mA/cm² or less, preferably 5mA/cm² or less, such a hybrid power source need not be fueled very often. Therefore, this hybrid power source is preferably with a fuel cell of low crossover current density such as the fuel cell of the invention. The fuel cell charges the battery and supplies the low power demand while the high power battery supplies the heavy loads. This small number of required fuel cells enables the use of a flat and thin fuel cell system.

15 The present invention provides such hybrid power sources that are fueled with the fuels of the present invention. Fueling such hybrid power sources with a solid fuel of the present invention will be most advantageous.

For example, to power a cellular phone it is possible to use a hybrid power source built of two thin fuel cells, connected in a series combination and fueled by liquid fuels of the invention such as EG or by a solid fuel of the invention, such as DMO, a DC to DC converter and a small high power lithium ion cell.

BRIEF DESCRIPTION OF THE DRAWINGS

25 In order to better understand the invention and to see how it may work in practice, several embodiments of the invention will now be described in detail, with reference to the accompanying drawings, in which:

Fig. 1 is a graph showing polarization curves of some fuels according to the present invention and some current art fuels; and

Fig. 2 is a schematic illustration of a solid feed organic fuel cell in accordance with the invention.

DETAILED DESCRIPTION OF SOME EMBODIMENTS

5 **Example 1: Obtaining polarization curves for several fuels**

A fuel cell was manufactured with the use of pure metal catalysts, instead of carbon supported catalysts. A cathodic catalyst ink was prepared by the following process:

10 A nano powder Pt (Pt black, purchased from "Johnson Matthey"), TeflonTM emulsion and NafionTM 5% solution were combined in the following weight proportions: 60%Pt, 25% Teflon emulsion and 15% Nafion. First the Pt powder and the Teflon emulsion were mixed by sonication for 15 minutes. After two sonication periods, the ink obtained was placed on a magnetic stirrer for at least one night.

15 An anodic catalyst ink was prepared by the following process: A Pt:Ru nano powder (Pt:Ru black 50% purchased from "Johnson Matthey") and PVDF were mixed in the following weight proportions: 91% catalyst powder and 9% PVDF. Propylene carbonate was added in an amount equal to 30-70% of the catalyst volume, then cyclopentanone was added and the ink obtained was stirred for at
20 least one night.

Preparation of the electrodes: the cathode catalyst ink was applied on teflonated TorayTM carbon fiber paper, to form 4 mg Pt/cm². The ink (in the form of a paste) was spread in layers, allowing each layer to dry for about one hour, before the next layer was applied. This operation was repeated until the
25 desired amount of catalyst was obtained. In the same way, the anode catalyst ink was applied on unteflonated TorayTM carbon fiber paper, until 5-10 mg catalyst/cm² was obtained. Both electrodes were washed with 3M sulfuric acid and then with water.

The cathode and the anode were placed on both sides of the PCM, with a thickness of 100-300 μm , parallel to each other and were hot pressed under a pressure of 10-70 Kg/cm^2 , at a temperature of 85-130°. Fig. 1 illustrates polarization curves for this kind of fuel cell under the following conditions: a solution of the fuel and 3M H_2SO_4 was circulated through the anode at a rate of 9ml/min. Oxygen was circulated past the cathode at a pressure of 0.25 atm. over the atmospheric pressure. The cell temperature was 65°C. The PCM was 300 micron thick, consisting of (V/V) 16% nanosize powder of SiO_2 , 24% PVDF and 60% pore volume, of 1.5 nm typical diameter. The cell demonstrated over 100 hours of stable operation at 0.4V. The fuels tested have been: methanol (1M), oxalic acid (0.1M with methanol 1M, Oxalic acid 0.1M, dimethyl oxalate 0.1M, ethylene glycol 0.5M, and glycerol 0.5M. (Of these, glycerol oxalic acid and methanol are not in accordance of the present invention.) As shown in the graph, under these conditions DMO and EG had the best performance. However, one should keep in mind that none of the conditions in this experiment was optimized, so that other concentrations and/or other catalysts could have resulted in qualitatively different observations.

Fuel utilization was determined by performing electrochemical titrations of 50 ml of fuel solution at constant voltage until the current dropped to 3 mA. It is estimated that at this current only a few percents of the fuel left not oxidized. The utilization was calculated by comparing the experimental capacity with the theoretical value. A further correction was made by extrapolation of the titration curves to zero current. This correction increases the utilization values by 3 to 6% (Table 1).

Fuel utilization at 0.2V was found to be 95% for DMO, 94% for EG and only 85% for methanol (see Table 1). At the more practical voltage of 0.4V, fuel utilization was found to be 89% for EG, 67% for DMO and 81% for methanol.

As the fuel does crossover to the cathode side, these high fuel utilization values suggest there is close to 100% fuel electro-oxidation.

Measurements of fuel crossover were carried out at several temperatures by feeding nitrogen instead of oxygen into the cathode compartment (at ambient pressure) and feeding organic fuel-acid solution into the anode compartment. Cell voltage was reversed; hydrogen was evolved at the fuel electrode while fuel that crossed over to the cathode side was oxidized. The current that flows at 1V was found to be the limiting current for oxidation of all fuels.

Table 2 summarizes the fuel crossover test results. The crossover current density depends on fuel permeability, temperature, concentration and on the total number of electrons involved in the oxidation. The crossover current density for 1M methanol (at 80°C) is double that of 1M EG and that of 0.25M DMO. However, when the number of electrons is taken into account and the fuel flux in terms of $\text{mol}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ (at 80°C and under diffusion-controlled conditions) is normalized to 1M fuel, it can be seen that the permeability (flux) of EG is one-third that of methanol while that of DMO is almost as large as that of methanol.

Table 1: Utilization comparison of different fuels.

	Number of electrons	Theoretical Capacity [Ah/g]	Utilization At 0.4V* [%]		Utilization At 0.2V* [%]	
			Exp.	Corr.	Exp.	Corr
Oxalic acid	2	0.43			91	
Methanol	6	5.03	79	81	82	85
Ethylene glycol	10	4.32	83	89	89	94
Dimethyl oxalate	14	3.18	64	67	93	95

*An average of at least two tests;

Exp. – experimental values; Corr. – corrected values, see text.

Table 2: Crossover of different fuels.

1. Fuel	Crossover test:			
	Temp. [°C]	Conc. [M]	Crossover current Density [A/cm ²]	Fuel flux* [mol·s ⁻¹ ·cm ⁻²] 1x10 ⁻⁸
Dimethyl oxalate	60	0.10	0.009	6.7
	60	0.25	0.025	7.4
	80	0.25	0.038	11
Ethylene glycol	80	0.5	0.019	3.9
	80	1.0	0.041	4.2
Methanol	80	1.0	0.076	13

* Normalized to 1M

5

Example 2: Application of fuels according to the invention to a Nafion™ based fuel cell

A fuel cell housing was fabricated from synthetic graphite plates purchased from Globetech Inc., in which a flow field was engraved.

10 The anode was formed using a platinum-ruthenium ink that was spread on a carbon fiber sheet commercially available from Toray™ paper. The catalyst layer consists of 15% Teflon (DuPont), 15% Nafion™ and 70% Pt-Ru nanopowder (Pt:Ru black 50% purchased from "Johnson Matthey"). Anode loading was 5mg/cm². The cathode used was a commercially available ELAT E-TEK™
 15 consisting of 4mg Pt/cm² and 0.6 mg nafion/cm². The anode and cathode were hot pressed to a 117 Nafion membrane, available from DuPont, to form the membrane electrode assembly (MEA) as described in Example 1.

After cooling the MEA was placed between the graphite flow field plates, a polypropylene sealing was inserted and the cell was assembled.

During operation, an aqueous solution of a fuel selected from oxalic acid, dimethyl oxalate, ethylene glycol, glycerol, in the concentration range of 0.1–0.5 M was circulated past the anode (with the use of a peristaltic Masterflex L/S Cole-Parmer Instrument Co. pump) at different flow rates from 4 to 15ml/min.

Oxygen was fed into the cathode chamber directly or through a water bubbler at an ambient pressure and at a rate of 7 to 40 ml/min. The cells were run at 60°C. The polarization curves were found to be similar to those of Figure 1.

Example 3. Solid feed organic fuel cell

Fig. 2 illustrates a solid feed organic fuel cell having a plastic case **501**, an anode **509**, a cathode **511** and a solid polymer electrolyte membrane **510**. The membrane **510** was a PCM of the kind described in WO99/44245, consisting of 12% SiO₂ 28% PVDF and 60% voids (to which the acid solution was introduced). The anode, cathode and MEA were prepared as in Example 1. The solid organic fuel is filled through the fuel hole **502** and sealed with a cork **503**. The fuel is dissolved in the tank and is absorbed through a hastalloy C-276 (Cabot) net **507** at a porous carbon cloth **508**. Carbon dioxide formed in the anode compartment is vented through an exhaust nozzle **504**. Since liquid fuel may leak through the exhaust nozzle, the nozzle is covered with a thin hydrophobic porous layer **506**. The hydrophobic layer is permeable to the gas only while the fuel solution remains in the tank. The cathode is open to air through a second hastalloy net **513**. In order to prevent the fuel leaking from the cathode side, the MEA is sealed with a gasket **512**. The second hastalloy net **513** is used also as a cover to the whole assembly. 200mg DMO were dissolved into the fuel tank, which contained 1M H₂SO₄ solution. The fuel cell delivered 30mA at 0.35V. The crossover current density was 2 mA/cm² at room temperature.

CLAIMS:

1. Organic compounds, selected from the group consisting of dimethyl oxalate, ethylene glycol, its oxalic, glyoxalic, and formic esters, glyoxylic
5 acid and its methyl esters, glyoxylic aldehyde, and poly(ethylene oxalate)
for use as fuels in non-alkaline fuel cells.
2. Organic compounds according to claim 1 selected from the group consisting of dimethyl oxalate, ethylene glycol, its formic acid ester, ethylene oxalate and poly(ethylene oxalate), and mixtures thereof, for use as
10 defined in claim 1.
3. Organic compounds according to claim 1, selected from the group consisting of ethylene glycol dimethyl oxalate and mixtures thereof for use as defined in claim 1.
4. Organic compounds according to claim 1, selected from the group
15 consisting of dimethyl oxalate, poly(ethylene oxalate) and mixtures thereof
for use as defined in claim 1.
5. Mixtures of Organic compounds according to any one of claims 1 to 4 with known fuels for the use defined in claim 1.
6. Mixtures according to claim 5 wherein said known fuel is methanol for
20 the use as defined in claim 1.
7. Compounds according to any one of claims 1 to 6 for the use defined in claim 1, wherein said fuel cell is an acidic electrolyte fuel cell.
8. Compounds according to any one of claims 1 to 6 for the use defined in claim 1, wherein said fuel cell has a proton conducting membrane.
- 25 9. A mixture according to claim 5, for use as defined in claim 7 or 8.
10. A direct oxidation fuel cell having an anode, a cathode, a proton conducting membrane disposed between said anode and said cathode, means for storing or supplying an organic fuel to the anode, and means for supplying oxygen to the cathode, wherein said organic fuel is selected from
30 the group consisting of dimethyl oxalate, ethylene glycol, its oxalic,

glyoxalic, and formic esters, glyoxylic acid and its methyl esters, glyoxylic aldehyde, and poly(ethylene oxalate).

11. A direct oxidation fuel cell according to claim 10 wherein said fuels are selected from the group consisting of dimethyl oxalate, ethylene glycol, its oxalic and formic acid esters, poly(ethylene oxalate), and mixtures thereof.
12. A direct oxidation fuel cell according to claim 11 wherein the fuel is selected from the group consisting of dimethyl oxalate, ethylene glycol, its formic acid ester, ethylene oxalate, poly(ethylene oxalate), and mixtures thereof.
13. A direct oxidation fuel cell according to claim 12 wherein the fuel is selected from the group consisting of dimethyl oxalate, ethylene glycol, and mixtures thereof.
14. A liquid feed direct oxidation fuel cell according to any one of claims 10 to 13, wherein said fuel cell is liquid feed.
15. A liquid feed direct oxidation fuel cell according to claim 13 wherein the fuel is selected from the group consisting of poly(ethylene oxalate), dimethyl oxalate, and mixtures thereof.
16. A liquid feed direct oxidation fuel cell according to any one of claim 14 or 15, further characterized in that the CO₂ produced during the operation thereof is released through a thin hydrophobic porous matrix placed in the anode compartment or in the fuel tank.
17. A direct oxidation fuel cell, having a cathode comprising an oxygen reduction catalyst and a fuel oxidation catalyst.
18. A direct oxidation fuel cell according to claim 17 wherein said fuel oxidation catalyst is selected from the group consisting of Pt-Ru, Pt-Sn, Pt-Ru-Sn, Pt-Ag-Ru, Pt-Os catalysts, and any combination thereof.
19. A direct oxidation fuel cell according to claim 18 wherein the ratio between the fuel oxidation catalyst to the oxygen reduction catalyst is between 1% to 50%, (w/w).

20. A direct oxidation fuel cell according to claim 19 wherein said ratio is between 5% to 20%, (w/w).
21. A direct oxidation fuel cell according to any one of claims 14 to 17, wherein said fuel is a mixture as defined in claim 5 or 6.
- 5 22. A method for evaluating the concentration of fuels in a solution, at a predetermined temperature, the fuels being compounds according to any one of claims 1 to 6, comprising the following steps:
- a) preparing calibration curves of crossover current vs. fuel concentration at said predetermined temperature in a given fuel cell;
 - 10 b) measuring the crossover current at said predetermined temperature in said given fuel cell; and
- evaluating the fuel concentration from the crossover current measured in step b) and the calibration curves prepared in step a).
23. A hybrid power source comprising at least one fuel cell according to any one of claims 10 to 21, a DC to DC converter, and a rechargeable battery.
- 15 24. A hybrid power source comprising at least one fuel cell according to claim 15, a DC to DC converter, and a rechargeable battery.

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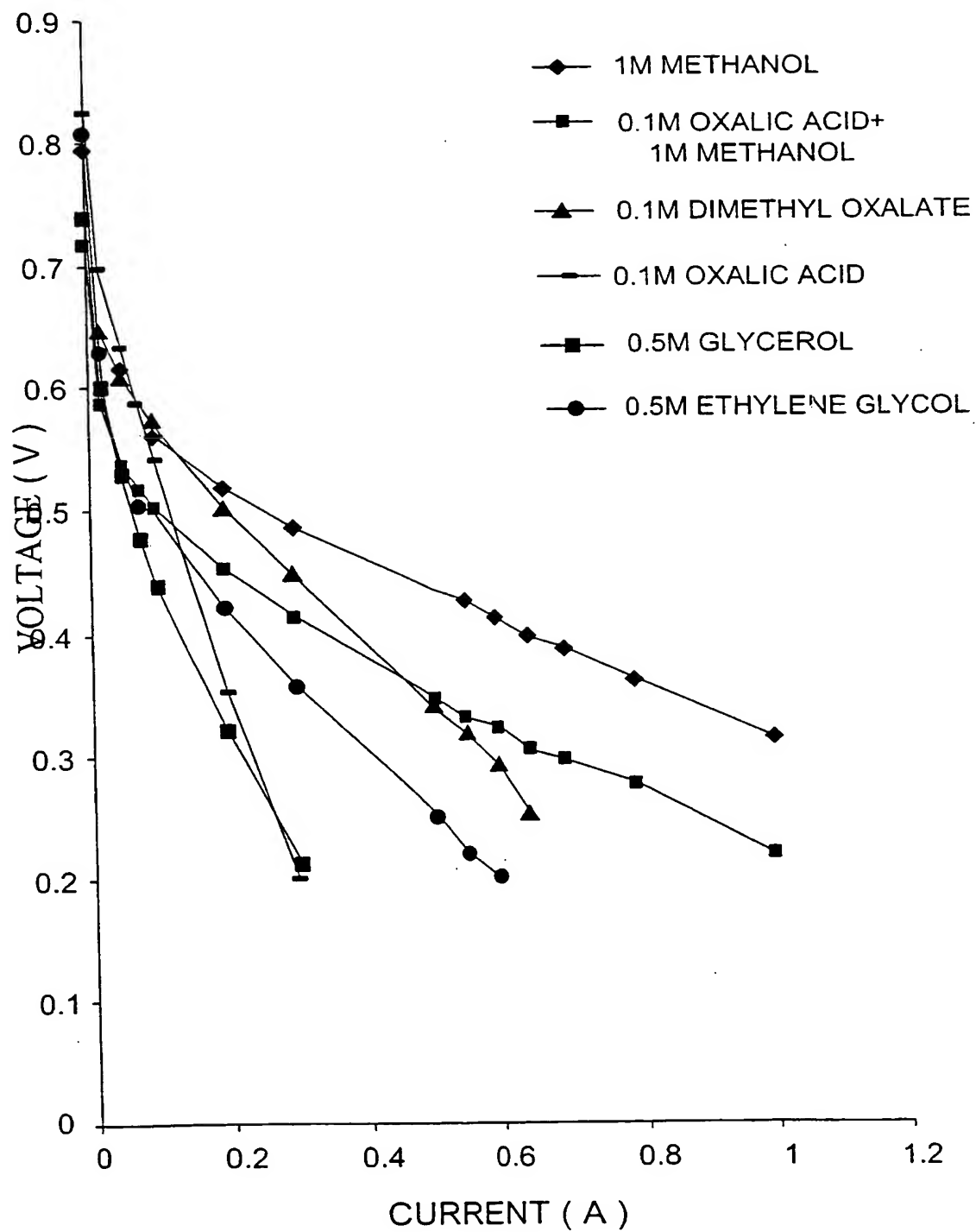


FIG. 1

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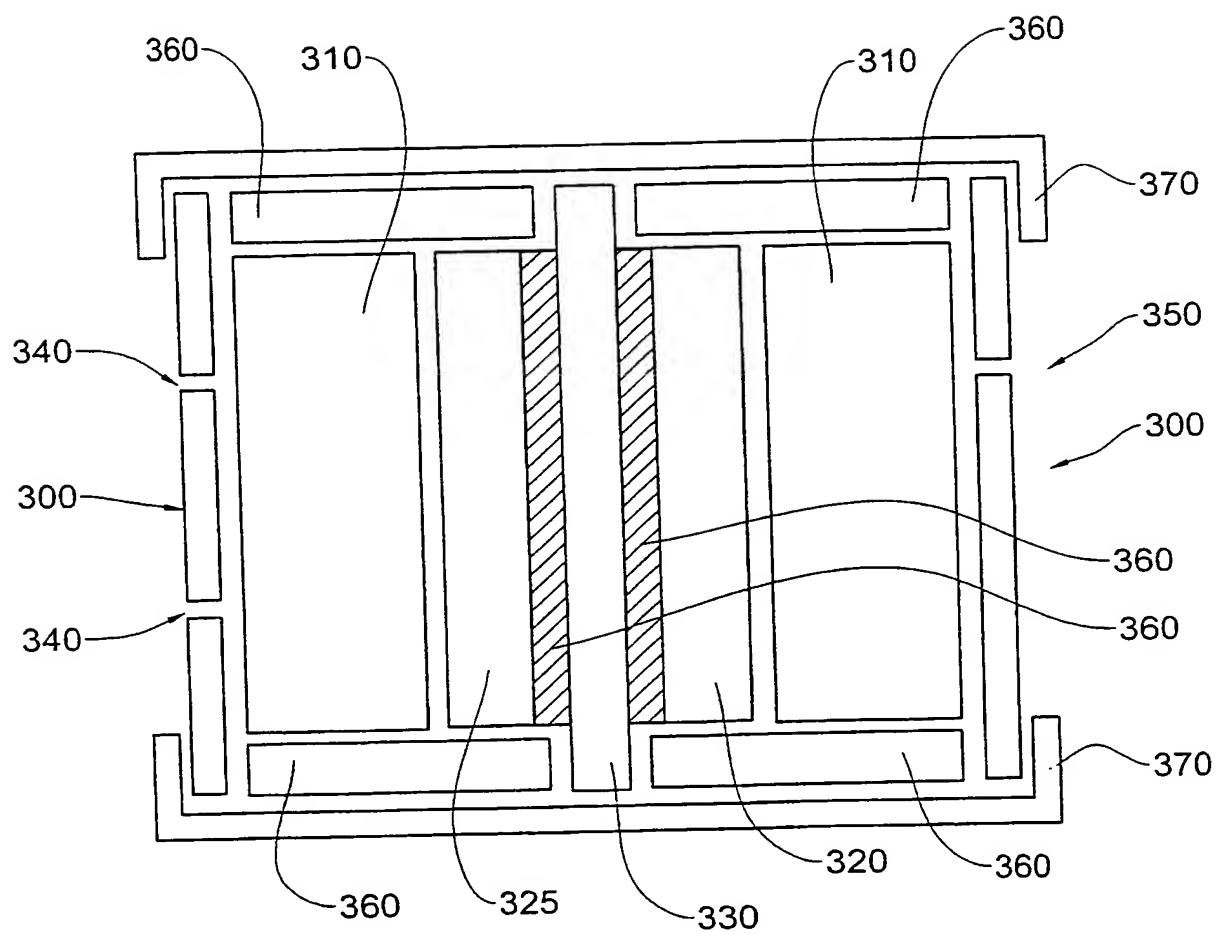


FIG. 2

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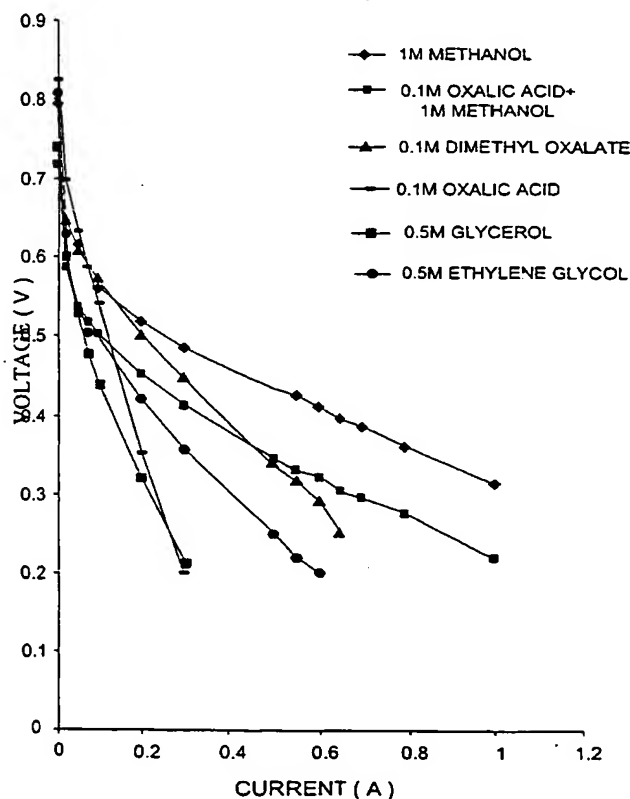
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(54) Title: FUELS FOR NON-ALKALINE FUEL CELLS



(57) Abstract: Disclosed are the use of dimethyl oxalate, ethylene glycol, its oxalic, glyoxalic, and formic esters, glyoxylic acid and its methyl esters, glyoxylic aldehyde, and poly(ethylene oxalate) for fueling fuel cells, fuel cells fueled by these compounds, a hybrid power source containing these fuel cells, and a method for evaluating their concentration in solution.

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(88) **Date of publication of the international search report:**
8 August 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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INTERNATIONAL SEARCH REPORT

Int. nat. Application No.

P L 01/00054

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M8/10 H01M8/08 H01M8/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	L.G.AUSTIN: "FUEL CELLS - A Review of Government-Sponsored Research, 1950-1964" 1967, NASA REPORT NO SP-120, NATIONAL AERONAUTICS AND SPACE ADMINISTRATION, WASHINGTON, D.C. XP002182766 cited in the application page 224, left-hand column, last paragraph -right-hand column, paragraph 1; table 15.1 --- -/--	1-4,7

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

14 November 2001

Date of mailing of the international search report

08.03.02

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
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Fax: (+31-70) 340-3016

Authorized officer

D'HONDT J.W.

INTERNATIONAL SEARCH REPORT

International Application No

F IL 01/00054

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>"ETUDE DE L'OXYDATION ELECTROCHIMIQUE DU GLYCOL ETHYLENIQUE SUR ELECTRODES DE PLATINE 1. ETUDE EXPERIMENTALE DES COURBES INTENSITE-POTENTIEL ET SELECTIONDES CONDITIONS OPERATOIRES ELECTROCHEMICAL OXIDATION AND WATER CONVERSION OF ETHYLENE GLYCOL APPLICATION TO FUEL CELLS"</p> <p>REVUE DE L'INSTITUT FRANCAIS DU PETROLE, EDITIONS TECHNIP. PARIS, FR, vol. XXIV, no. 6, June 1969 (1969-06), pages 728-758, XP001039549</p> <p>ISSN: 1294-4475</p> <p>abstract</p> <p>page 733 -page 735</p> <p>---</p>	1-3,7
X	<p>GONZALES M J ET AL: "ELECTROCATALYTIC OXIDATION OF SMALL CARBOHYDRATE FUELS AT PT-SN MODIFIED ELECTRODES"</p> <p>JOURNAL OF PHYSICAL CHEMISTRY. B, MATERIALS, SURFACES, INTERFACES AND BIOPHYSICAL, WASHINGTON, DC, US, vol. 102, no. 49, 1998, pages 9881-9890, XP001039555</p> <p>ISSN: 1089-5647</p> <p>abstract</p> <p>page 9881, left-hand column, paragraph 1 figures 4,5</p> <p>page 9885, left-hand column, paragraph 2 -right-hand column, paragraph 1</p> <p>---</p>	1-3
X	<p>OCON P ET AL: "THE ELECTROOXIDATION OF GLYOXYLIC ACID ON UPD MODIFIED GOLD ELECTRODES IN ACIDIC MEDIUM"</p> <p>BULLETIN OF ELECTROCHEMISTRY, CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE,, IN, vol. 15, no. 1, January 1999 (1999-01), pages 34-41, XP001039554</p> <p>ISSN: 0256-1654</p> <p>abstract</p> <p>page 34, left-hand column, paragraph 1</p> <p>---</p>	1
X	<p>PATTABIRAMAN R ET AL: "PLATINUM ALLOY BIMETALLIC CATALYSTS FOR FUEL CELLS"</p> <p>BULLETIN OF ELECTROCHEMISTRY, CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE,, IN, vol. 15, no. 9/10, September 1999 (1999-09), pages 394-399, XP001039553</p> <p>ISSN: 0256-1654</p> <p>abstract</p> <p>page 394, left-hand column, paragraph 1 -right-hand column, paragraph 1</p> <p>---</p> <p>-/--</p>	1-3

INTERNATIONAL SEARCH REPORT

International Application No

F . IL 01/00054

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HAMANN, C. H. ET AL: "Electric current from the direct conversion of low molecular weight carbon, hydrogen, oxygen compounds" retrieved from STN Database accession no. 88:123741 CA XP002182767 abstract & J. POWER SOURCES (1976), 1(2), 141-57, 1976, -----	1
A	US 4 650 729 A (TAKAGI YASUO ET AL) 17 March 1987 (1987-03-17) column 2, line 31 - line 55; figure 2 -----	23
A	GB 2 281 642 A (IMRA EUROP SA) 8 March 1995 (1995-03-08) claim 1; figure 1 -----	23,24
A	US 4 562 123 A (DOI RYOUTA ET AL) 31 December 1985 (1985-12-31) column 7, line 18; claim 1; figure 1 -----	16
A	US 5 599 638 A (PRAKASH G K SURYA ET AL) 4 February 1997 (1997-02-04) cited in the application claims 1,7 -----	10,14
A	WANG J ET AL: "EVALUATION OF ETHANOL, 1-PROPANOL, AND 2-PROPANOL IN A DIRECT OXIDATION POLYMER-ELECTROLYTE FUEL CELL" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY. MANCHESTER, NEW HAMPSHIRE, US, vol. 142, no. 12, 1 December 1995 (1995-12-01), pages 4218-4224, XP000551129 ISSN: 0013-4651 abstract -----	10,14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL 01/00054

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-16,22,23(part),24

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-16, 22, 23(partially), 24

Organic compounds as enumerated in claim 1 for use as fuels in non-alkaline fuel cells, direct oxidation fuel cell with proton conductive conducting membrane and said organic compounds as fuel, evaluating the concentration of said fuels by preparing calibration curves of crossover current vs. fuel concentration of said fuels and measuring crossover current, hybrid power source comprising such direct oxidation fuel cell with proton conducting membrane, a DC/Dc converter and a rechargeable battery

2. Claims: 17-21 and 23 if dependent from 17

A direct oxidation fuel cell having a cathode comprising a oxygen reduction catalyst and a fuel oxidation catalyst and a hybrid power source comprising such fuel cell, a DC/DC converter and a rechargeable battery

INTERNATIONAL SEARCH REPORT

In national Application No

PCT/IL 01/00054

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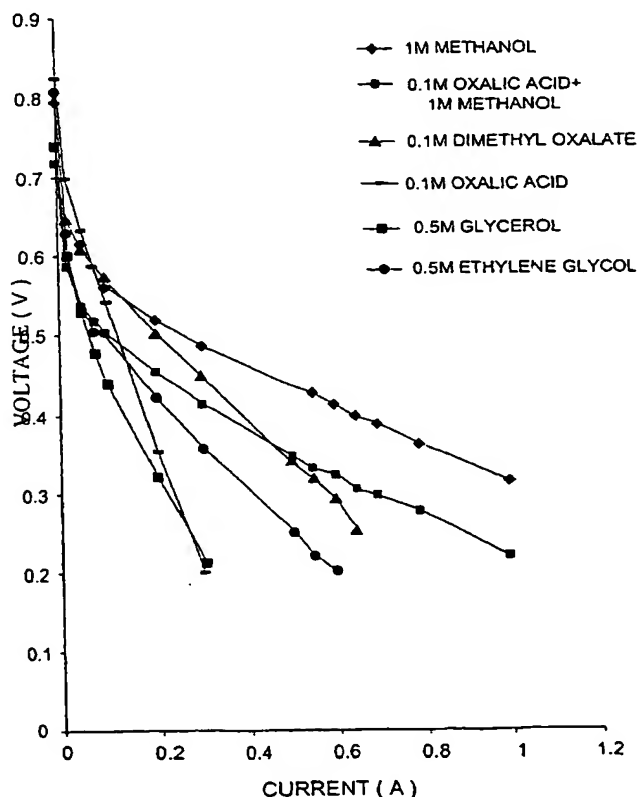
(71) Applicant (for all designated States except US): RAMOT
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[Continued on next page]

(54) Title: FUELS FOR NON-ALKALINE FUEL CELLS



(57) Abstract: Disclosed are the use of dimethyl oxalate, ethylene glycol, its oxalic, glyoxalic, and formic esters, glyoxylic acid and its methyl esters, glyoxylic aldehyde, and poly(ethylene oxalate) for fueling fuel cells, fuel cells fueled by these compounds, a hybrid power source containing these fuel cells, and a method for evaluating their concentration in solution.

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(81) **Designated States (national):** AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

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Date of publication of the revised international search report:

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(15) **Information about Correction:**

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IL 01/00054

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M8/10 H01M8/08 H01M8/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, INSPEC, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	L.G.AUSTIN: "FUEL CELLS - A Review of Government-Sponsored Research, 1950-1964" 1967, NASA REPORT NO SP-120, NATIONAL AERONAUTICS AND SPACE ADMINISTRATION, WASHINGTON, D.C. XP002182766 cited in the application page 224, left-hand column, last paragraph -right-hand column, paragraph 1; table 15.1 --- -/-	1-4,7

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- *A* document defining the general state of the art which is not considered to be of particular relevance
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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

5 July 2002

Date of mailing of the international search report

17. 07. 02

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Authorized officer

D'hondt, J

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>"ETUDE DE L'OXYDATION ELECTROCHIMIQUE DU GLYCOL ETHYLENIQUE SUR ELECTRODES DE PLATINE 1. ETUDE EXPERIMENTALE DES COURBES INTENSITE-POTENTIEL ET SELECTION DES CONDITIONS OPERATOIRES ELECTROCHEMICAL OXIDATION AND WATER CONVERSION OF ETHYLENE GLYCOL APPLICATION TO FUEL CELLS"</p> <p>REVUE DE L'INSTITUT FRANCAIS DU PETROLE, EDITIONS TECHNIP. PARIS, FR, vol. XXIV, no. 6, June 1969 (1969-06), pages 728-758, XP001039549</p> <p>ISSN: 1294-4475</p> <p>abstract</p> <p>page 733 -page 735</p>	1-3,7
X	<p>GONZALES M J ET AL: "ELECTROCATALYTIC OXIDATION OF SMALL CARBOHYDRATE FUELS AT PT-SN MODIFIED ELECTRODES"</p> <p>JOURNAL OF PHYSICAL CHEMISTRY. B, MATERIALS, SURFACES, INTERFACES AND BIOPHYSICAL, WASHINGTON, DC, US, vol. 102, no. 49, 1998, pages 9881-9890, XP001039555</p> <p>ISSN: 1089-5647</p> <p>abstract</p> <p>page 9881, left-hand column, paragraph 1 figures 4,5</p> <p>page 9885, left-hand column, paragraph 2 -right-hand column, paragraph 1</p>	1-3
X	<p>OCON P ET AL: "THE ELECTROOXIDATION OF GLYOXYLIC ACID ON UPD MODIFIED GOLD ELECTRODES IN ACIDIC MEDIUM"</p> <p>BULLETIN OF ELECTROCHEMISTRY, CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE,, IN, vol. 15, no. 1, January 1999 (1999-01), pages 34-41, XP001039554</p> <p>ISSN: 0256-1654</p> <p>abstract</p> <p>page 34, left-hand column, paragraph 1</p>	1
X	<p>PATTABIRAMAN R ET AL: "PLATINUM ALLOY BIMETALLIC CATALYSTS FOR FUEL CELLS"</p> <p>BULLETIN OF ELECTROCHEMISTRY, CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE,, IN, vol. 15, no. 9/10, September 1999 (1999-09), pages 394-399, XP001039553</p> <p>ISSN: 0256-1654</p> <p>abstract</p> <p>page 394, left-hand column, paragraph 1 -right-hand column, paragraph 1</p> <p style="text-align: center;">-/-</p>	1-3

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; HAMANN, C. H. ET AL: "Electric current from the direct conversion of low molecular weight carbon, hydrogen, oxygen compounds" retrieved from STN Database accession no. 88:123741 CA XP002182767 abstract & J. POWER SOURCES (1976), 1(2), 141-57, 1976,</p>	1
A	<p>US 4 650 729 A (TAKAGI YASUO ET AL) 17 March 1987 (1987-03-17) column 2, line 31 - line 55; figure 2</p>	23
A	<p>GB 2 281 642 A (IMRA EUROP SA) 8 March 1995 (1995-03-08) claim 1; figure 1</p>	23,24
A	<p>US 4 562 123 A (DOI RYOUTA ET AL) 31 December 1985 (1985-12-31) column 7, line 18; claim 1; figure 1</p>	16
A	<p>US 5 599 638 A (PRAKASH G K SURYA ET AL) 4 February 1997 (1997-02-04) cited in the application claims 1,7</p>	10,14
A	<p>WANG J ET AL: "EVALUATION OF ETHANOL, 1-PROPANOL, AND 2-PROPANOL IN A DIRECT OXIDATION POLYMER-ELECTROLYTE FUEL CELL" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY. MANCHESTER, NEW HAMPSHIRE, US, vol. 142, no. 12, 1 December 1995 (1995-12-01), pages 4218-4224, XP000551129 ISSN: 0013-4651 abstract</p>	10,14
A	<p>US 3 357 861 A (HUNGER HERBERT F) 12 December 1967 (1967-12-12) column 3, line 27 - line 48; claim 1</p>	17
	-/-	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	OKAMOTO T: "Methanol fuel cells" STN CHEMICAL ABSTRACTS, XX, XX, vol. 128, no. 13, 30 March 1998 (1998-03-30), XP002141901 -& PATENT ABSTRACTS OF JAPAN vol. 1998, no. 06, 30 April 1998 (1998-04-30), & JP 10 040936 A (HONDA MOTOR CO LTD), 13 February 1998 (1998-02-13) abstract	17
A	EP 0 090 358 A (HITACHI LTD) 5 October 1983 (1983-10-05) claims 1,2,11-13	17
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL 01/00054

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-16, 22, 23(partially), 24

Organic compounds as enumerated in claim 1 for use as fuels in non-alkaline fuel cells, direct oxidation fuel cell with proton conductive conducting membrane and said organic compounds as fuel, evaluating the concentration of said fuels by preparing calibration curves of crossover current vs. fuel concentration of said fuels and measuring crossover current, hybrid power source comprising such direct oxidation fuel cell with proton conducting membrane, a DC/Dc converter and a rechargeable battery

2. Claims: 17-21 and 23 if dependent from 17

A direct oxidation fuel cell having a cathode comprising a oxygen reduction catalyst and a fuel oxidation catalyst and a hybrid power source comprising such fuel cell, a DC/DC converter and a rechargeable battery

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/IL 01/00054

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
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